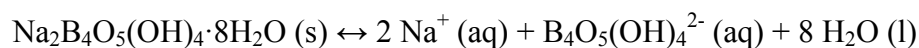


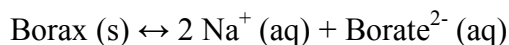
Thermodynamics of Borax Dissolution

Introduction

Borax ($\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$) is a mineral found in dry lake beds of the southwest United States. It is used as a preservative, as a flux for solder, in the manufacture of glass, and as a laundry detergent. The latter application is somewhat surprising since borax is not very soluble in water. The dissolution reaction is:



This reaction can be simplified to:



When solid borax is placed in water, the solid will dissolve until saturation is reached. At saturation, the product of the concentrations of sodium ion and borate equal a constant. The mathematical expression for this sparingly soluble salt in water is $K_{\text{sp}} = [\text{Na}^+]^2[\text{Borate}^{2-}]$ where the subscript on the equilibrium constant serves as an indicator that the reactant is a solid. The brackets denote molarity and the superscripts to each concentration equal the stoichiometric coefficients from the balanced equation.

The change in Gibb's free energy at standard temperature and pressure, ΔG° , is related to the equilibrium constant for the reaction by the equation:

$$\Delta G^\circ = RT \ln K_{\text{sp}}$$

The change in Gibb's free energy is also a function of the change in enthalpy, ΔH° , and the entropy, ΔS° , for this reaction:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

ΔH° indicates the amount of heat absorbed or released during the reaction and ΔS° represents the amount of molecular disorder created or removed during the reaction at standard temperature and pressure. Note that the temperature is in Kelvin. Setting the previous two equations equal to each other gives:

$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K_{\text{sp}} \rightarrow \ln K_{\text{sp}} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

The three thermodynamic parameters (ΔG° , ΔH° , and ΔS°) can be determined from measurement of K_{sp} at several temperatures. A plot of $\ln K_{\text{sp}}$ (y-axis) versus $1/T$ (x-axis) should yield a straight

line whose slope is equal to $-\Delta H^\circ/R$ and whose intercept $\Delta S^\circ/R$. Again note that temperature will be measured in $^\circ\text{C}$ but must be converted to Kelvin for this plot.

How will the K_{sp} values be determined for this reaction? The borate ion is a base and its concentration can be found by titration with a standardized HCl solution according to the neutralization equation:



where H_3BO_3 is the chemical formula for boric acid. According to the equilibrium expression for borate, if the borate ion concentration is given by x , then the sodium ion concentration is $2x$. The K_{sp} value at a given temperature becomes: $K_{\text{sp}} = [2x]^2[x] = 4x^3$.

In this experiment, three chemically important thermodynamics parameters for the dissolution of borax in water will be measured. The molarity of the borate ion will be determined through the titration with a standardized HCl solution at different temperatures. The data from the concentration as a function of temperature will be used to compute ΔG° , ΔH° , and ΔS° .

Prelab Questions

- 1) How will the concentration of borate ion generated from dissolution of borax be determined?
- 2) What is methyl orange and what is its purpose in this experiment?
- 3) The solubility of borax will be determined as a function of temperature. How many different temperatures must be examined to determine the values of ΔH° and ΔS° for this reaction?

Procedure

- 1) Obtain three beakers and label each as "Room Temp, Cold Temp, and Hot Temp."
- 2) Mass out 3.0xx grams of solid borax into each beaker. Add 50 mL of DI water into each beaker.
- 3) Set the "Room Temp" beaker on the lab bench for 15 minutes, stirring occasionally.
- 4) Place the "Cold Temp" beaker into an ice-water bath for 25-30 minutes, stirring occasionally.
- 5) Place the "Hot Temp" beaker on a hot plate and heat the solution to no more than 50°C for 25-30 minutes, stirring occasionally.
- 6) Each solution needs to reach equilibrium before titrating. There MUST be undissolved borax present at equilibrium. After the time frame for each beaker, if there is no undissolved borax present, add extra borax.
- 7) While the borax solutions are reaching equilibrium, set up the burette:
 - (a) Obtain a burette and rinse with 5-10 mL of DI water.
 - (b) Then rinse the burette with 5-10 mL of $\sim 0.10 \text{ M HCl}$.

- (c) Fill the burette completely with ~0.10 HCl, recording the exact concentration. Record the initial volume.
- 8) After equilibrium has been reached in the “Room Temp” beaker, allow the excess borax to settle to the bottom of the beaker. Transfer 5.0 mL of solution to an Erlenmeyer flask.
 - 9) Add a few drops of methyl orange and the solution should turn yellow.
 - 10) Titrate the contents of the “Room Temp” flask to a yellow-orange endpoint. Record the final volume of HCl to two decimal places.
 - 11) Remove the “Cool Temp” and “Hot Temp” beakers from the ice-water bath and hot plate, respectively. Record the temperature of each solution.
 - 12) Transfer 5.0 mL of each solution to an Erlenmeyer flask.
 - 13) Repeat steps 9-10 with the “Cool Temp” and “Hot Temp” beakers. However, the flasks need to cool to room temperature before titrating.
 - 14) Dispose of all chemicals down the sink with water.

Results

[HCl] = _____

	Room Temperature	Cold Temperature	Hot Temperature
Mass of Borax (g)			
Temperature (°C)			
Temperature (K)			
Initial Volume			
Final Volume			
Moles of HCl			
Moles of Borate ²⁻			
Molarity of Borate ²⁻			
K _{sp}			
ΔG			

Calculations/Postlab Questions

- 1) From the moles of acid needed to neutralize the borax and the stoichiometric relationship between borate ion and HCl, calculate the moles of borate ion that was present for each temperature.
- 2) Calculate the molarity of borate ion in the 5.0 mL sample for each temperature.

- 3) Calculate the K_{sp} for each temperature.
- 4) Calculate the ΔG for each temperature, using the appropriate equation from the Introduction.
- 5) Plot $\ln K_{sp}$ (y-axis) versus $1/T$ (x-axis) and plot a linear regression line (trendline) with the equation. Note: include a copy of your graph in your lab report.
- 6) Using the slope and y-intercept from this line equation, calculate the ΔH° and ΔS° , respectively, for this reaction.
- 7) Using your experimentally determined values of ΔH° and ΔS° , calculate the ΔG° for this reaction.
- 8) A student allowed all the borax in the beaker to dissolve before measuring the concentration of borate ion in solution. Will the calculated K_{sp} be larger or smaller than one calculate from incomplete dissolution? Explain.
- 9) A student was unable to visualize the yellow-orange endpoint of the titration. The volume HCl recorded was consistently 15% higher than it should have been. What impact will this have on the measured values of ΔH° and ΔS° ? Explain.

* Adapted from “Thermodynamics of Borax Dissolution”—Bottomley, L; Bottomley, L.A.; *Chem 1211K/1212K: Laboratory Manual*, 2011-2012, p 211-219.